

# Carbon clusters near the crossover to fullerene stability

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The thermodynamic stability of structural isomers of  $C_{24}$ ,  $C_{26}$ ,  $C_{28}$  and  $C_{32}$ , including fullerenes, is studied using density functional and quantum Monte Carlo methods. The energetic ordering of the different isomers depends sensitively on the treatment of electron correlation. Fixed-node diffusion quantum Monte Carlo calculations predict that a  $C_{24}$  isomer is the smallest stable graphitic fragment and that the smallest stable fullerenes are the  $C_{26}$  and  $C_{28}$  clusters with  $C_{2v}$  and  $T_d$  symmetry, respectively. These results support proposals that a  $C_{28}$  solid could be synthesized by cluster deposition.

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Since the discovery of the fullerene  $C_{60}$  [1], the study of carbon clusters has revealed a rich variety of physical and chemical properties. Fullerene clusters may now be synthesised in macroscopic quantities, but despite many experimental and theoretical advances the detailed energetics of these systems are not yet fully understood. The question “which is the smallest stable fullerene?” remains both interesting and contentious due to the sensitivity of cluster formation to experimental conditions and the challenges posed to theoretical methods by system size and the high accuracy required. In this Letter we report very accurate calculations of the relative energies of  $C_{24}$ ,  $C_{26}$ ,  $C_{28}$  and  $C_{32}$  clusters, and identify the smallest stable fullerenes.

The number of low-energy candidate structures can be large, even for quite small clusters, precluding exhaustive theoretical searches with highly accurate but computationally expensive methods. In practice, a hierarchy of methods of increasing accuracy and computational cost must be used. The first step is to select candidate structural isomers via empirical methods based on bond counting and geometric “rules” such as “minimize the number of adjacent pentagons” [2]. Quantum mechanical calculations based on tight-binding and density functional theory (DFT) methods can then be used to refine the selection. To finally establish the energetic ordering of different isomers, highly accurate calculations must be performed. Quantum chemical methods, such as coupled cluster (CC) calculations [3], are potentially highly accurate, but are severely limited by the size of basis set that is computationally affordable in these systems. Quantum Monte Carlo (QMC) methods give an accurate treatment of electron correlation which, combined with an absence of basis set error, favorable scaling with system size and suitability for parallel computation, renders them ideal for these studies. QMC calculations have reproduced experimental binding energies of small hydrocarbons to within 1% [4]. Using the techniques described below we have calculated the cohesive energy of bulk diamond, obtaining values of 7.36(1) and 7.46(1) eV per atom in variational Monte Carlo (VMC) and diffusion Monte Carlo

(DMC), respectively, which are in very good agreement with the experimental value of 7.37 eV.

Carbon clusters are particularly challenging to model accurately due to the wide range of geometries and the occurrence of single, double, and triple bonds. These differences result in a non-cancellation of errors in relative energies, exaggerating any errors due to approximations involved in electronic structure methods. Despite these potential difficulties, carbon clusters have been extensively studied using methods such as tight-binding, density functional, quantum chemical and QMC [4–8]. The need for high accuracy calculations with a sophisticated treatment of electron correlation has been clearly illustrated by several previous studies. Grossman *et al.* [4] have performed diffusion Monte Carlo calculations for  $C_{20}$  clusters, finding that the fullerene is not energetically stable. A DFT study of  $C_{20}$  isomers showed that the local density approximation (LDA) [9] and the BLYP gradient-corrected functional [10] gave different energy orderings for the sheet, bowl and fullerene structures, with neither agreeing with that of DMC [4]. Jensen *et al.* [11] made calculations for the monocyclic ring and fullerene isomers of  $C_{24}$  which demonstrated significant differences between the predictions of the LDA, gradient corrected and hybrid density functionals. These authors also performed second-order Møller-Plesset and CC calculations, but with a limited basis set, concluding that the fullerene is lower in energy than the ring. Raghavachari *et al.* [12] and Martin *et al.* [13] studied seven isomers of  $C_{24}$  using DFT, but obtained conflicting energetic orderings.

For clusters containing between 20 and 32 atoms, three classes of isomer are energetically competitive: fullerenes, planar or near-planar sheets and bowls, and monocyclic rings. The smallest possible fullerene, defined as a closed cage containing only pentagonal and hexagonal faces [14], consists of 20 atoms. However, the smallest fullerenes most commonly identified by time of flight and mass spectroscopy measurements are the  $C_{30}$  and  $C_{32}$  clusters [15–17]. Rings are found to dominate up to approximately 28 carbon atoms under typical experimental conditions, and fullerenes are mostly observed for larger

clusters, although other structures are also present (see for example, Ref. [17]). In this work we present a QMC study of five isomers of  $C_{24}$ , three of  $C_{26}$  and  $C_{28}$ , and two of  $C_{32}$ , thereby covering the range of masses from where the fullerene is clearly predicted to be unstable to where a fullerene is clearly observed. This enables us to predict the smallest energetically stable fullerene.

We apply the diffusion quantum Monte Carlo method [18,19] in which the imaginary time Schrödinger equation is used to evolve an ensemble of electronic configurations towards the ground state. The “fixed node approximation” is central to this method; the nodal surface of the exact fermionic wave function is approximated by that of a guiding wave function. Core electrons were modeled by an accurate norm-conserving pseudopotential [20], and the non-local energy was evaluated stochastically within the locality approximation [21]. We used Slater-Jastrow guiding wave functions consisting of the product of a sum of Slater determinants of single-particle orbitals obtained from CRYSTAL95 [22] or Gaussian94 [23] with a Jastrow correlation factor [24]. Optimized uncontracted valence Gaussian basis sets of four  $s$ , four  $p$  and one  $d$  function were used to represent the single-particle orbitals. Jastrow factors of up to 80 parameters were optimized using efficient variance minimization techniques [25,26], yielding 75-90% of the DMC correlation energy.

We relaxed the structures by performing highly converged density functional calculations. The geometries were obtained from all-electron calculations [23] using the B3LYP hybrid functional [27] and Dunning’s cc-pVDZ basis set [28], which has been found to be an accurate and affordable combination [13,29,30]. To assess the sensitivity of the total energies to the geometries, we compared the energies of the fully relaxed ring and  $D_6$  fullerene isomers of  $C_{24}$  (see Fig. 1) using the BLYP and B3LYP functionals. The functionals give significantly different energetic orderings, but the differences between the geometries are small - less than 0.03 angstroms in bond lengths and 0.4 degrees in bond angles. The relative energies of these structures changed by a maximum of 0.27 eV for each of the functionals investigated. The relative energies are therefore rather insensitive to the functional used to obtain the geometries, but are more sensitive to the functional used to calculate the energies. These changes are small compared with the overall range of energies, but some changes in the orderings of the isomers closest in energy could occur.

We considered the following isomers of  $C_{24}$ , as depicted in Fig. 1: a polyacetylenic monocyclic ring, a flat graphitic sheet, a bowl-shaped structure with one pentagon, a caged structure with a mixture of square, pentagonal and hexagonal faces, and a fullerene. Other candidate structures, such as bicyclic rings and a 3-pentagon bowl were excluded on the grounds that DFT calculations using several different functionals have shown them to be significantly higher in energy [12,13]. As well as DMC

calculations we have also performed DFT calculations using the LDA, two gradient corrected functionals (PBE [31] and BLYP) and the B3LYP functional. The results shown in Fig. 1 confirm that the treatment of electron correlation has a profound effect on the relative energies. All of the functionals give different energetic orderings, and none gives the same ordering as DMC. The graphitic sheet is placed lowest in energy by DMC, in agreement with each of the functionals except BLYP, which places the ring lowest in energy. The low energy of the  $C_{24}$  graphitic sheet is expected because the structure accommodates a large number (7) of hexagonal rings without significant strain. This structure is predicted to be the smallest stable graphitic fragment. Both DMC and the DFT approaches find the  $C_{24}$  fullerene to be unstable.

Three isomers of  $C_{26}$  were considered: a cumulenic monocyclic ring, a graphitic sheet with one pentagon and a fullerene of  $C_{2v}$  symmetry (Fig. 2). Few studies of the  $C_{26}$  fullerene have been made, in part due to the high strains evident in its structure [14]. Recently Torelli and Mitáš have demonstrated the importance of using multi-determinant trial wave functions to describe aromaticity in  $4N+2$  carbon rings [32]. We have tested this for the  $C_{26}$  ring, using a 43 determinant trial wave function obtained from a CI singles-doubles calculation. The multi-determinant wave function gave a slightly lower DMC energy than the single determinant wave function, by approximately 0.5 eV, confirming that CI wave functions can have better nodal surfaces than HF wave functions. The ring and sheet-like isomers are close in energy, but the fullerene is approximately 2.5 eV below these isomers and is therefore predicted to be the smallest stable fullerene. Small changes in the geometries are highly unlikely to change this conclusion.

Three  $C_{28}$  isomers were investigated: a monocyclic ring, a graphitic sheet and a fullerene of  $T_d$  symmetry (Fig. 3). Other bowl and sheet-like structures were excluded on energetic grounds [30]. Spin-polarized DFT calculations show the ground state of the  $T_d$  symmetry fullerene to be a spin-polarized  $^5A_2$  state. DMC predicts that this spin-polarized fullerene is the lowest energy isomer of  $C_{28}$ , and this is supported by each of the functionals except BLYP. The spin-polarized fullerene has four unpaired electrons and is therefore highly reactive. This property has been exploited in atom trapping experiments in which fullerenes containing single four-valent atoms,  $C_{28}M$ , have been prepared by laser vaporization of a graphite- $MO_2$  ( $M = Ti, Zr, Hf$  or  $U$ ) composite rod [33]. Our prediction that the fullerene is the most stable isomer of  $C_{28}$  indicates that isolated fullerenes might be readily produced. This would facilitate investigations of  $C_{28}$  fullerene solids, which have been discussed but not yet produced [33,34], although this route may be hampered by the chemical reactivity of the fullerene. (A  $C_{36}$  fullerene solid has been reported [35].)

Our DFT and DMC results for  $C_{28}$  (Fig. 3) again high-

light a wide variation between different DFT functionals. The LDA and B3LYP functionals predict the same ordering as DMC, but the PBE and BLYP functionals give different orderings. The DMC data strongly indicates that the  $T_d$  fullerene is the most stable  $C_{28}$  isomer at zero temperature. The fullerene has the lowest DMC energy in both spin-polarized and non spin-polarized calculations, and is substantially more stable than the sheet and ring. Small changes in the geometries are therefore unlikely to change this ordering.

Our DMC calculations for the  $C_{32}$  monocyclic ring and fullerene show that the fullerene is 8.4(4) eV per molecule lower in energy, which is consistent with the observation of a large abundance of  $C_{32}$  fullerenes in a recent cluster experiment [15]. In Fig. 4 we plot the DMC binding energies per atom of all the ring and fullerene structures considered. The binding energies of the fullerenes rise much more rapidly with cluster size than those of the rings because of the large amount of strain in the smaller fullerenes. The DMC binding energy of the  $C_{32}$  fullerene is approximately 1 eV per atom less than the experimental binding energy of  $C_{60}$ .

Our DFT and DMC results highlight several important trends in the relative performance of the different functionals. The overall quality of a functional for the clusters is best judged by the agreement with the DMC data for the overall *shapes* of the relative energy data of Figs. 1-3. The best agreement is given by the PBE and B3LYP functionals, with the LDA being slightly inferior and the BLYP functional being worst. The tendency of the LDA to favor structures of high average coordination and for the BLYP functional to favor structures of low average coordination is consistent with the results for  $C_{20}$  reported by Grossman *et al.* [4].

The final test of our predictions must lie with experiment. It is clear that the actual abundances of different clusters depend sensitively on experimental conditions. Analysis of the stability of clusters against fragmentation, growth and other chemical reactions is complicated. One key issue is that the clusters are formed at temperatures of order 1000K and therefore the vibrational contributions to the free energy can be significant. Fortunately, a simple picture emerges from computations of vibrational properties [12,13,30]. Fullerenes are relatively rigid and have higher vibrational free energies than rings, which have many low-lying vibrational modes. Vibrational effects therefore tend to favor the ring isomers at high temperatures. However, according to our DMC calculations the  $C_{26}$  and  $C_{28}$  fullerenes are several eV per cluster lower in energy than the other isomers, so that significant amounts of fullerene could exist at the temperatures of formation. If thermodynamic stability alone were to determine which cluster sizes were observed then only the largest fullerenes would ever be observed, but in a recent experiment the abundance of the  $C_{32}$  fullerene was found to be *greater* than  $C_{60}$  [15]. There is more evi-

dence that thermodynamic stability to rearrangements of clusters of a particular size are important in determining which isomers are observed. For example, in the experimental study of Ref. [15], fullerenes were mostly observed for clusters containing more than about 30 carbon atoms, while for smaller clusters mostly rings were formed. This crossover is close to the critical size for fullerene stability of 26-28 atoms predicted by our DMC calculations.

In conclusion, performing accurate calculations of the relative energies of carbon clusters is a severe test of electronic structure methods because of the widely differing geometries and the occurrence of single, double and triple bonds. In our DMC calculations for  $C_{24}$ , the lowest energy isomer is a graphitic sheet, which is expected to be the smallest stable graphitic fragment. We predict that the smallest energetically stable fullerenes are the  $C_{2v}$  symmetry  $C_{26}$  cluster and the spin polarized  $^5A_2$  state of the  $T_d$  symmetry  $C_{28}$  cluster. This prediction lends weight to recent proposals that a  $C_{28}$  solid [33,34] could be synthesized by surface deposition of  $C_{28}$  fullerenes.

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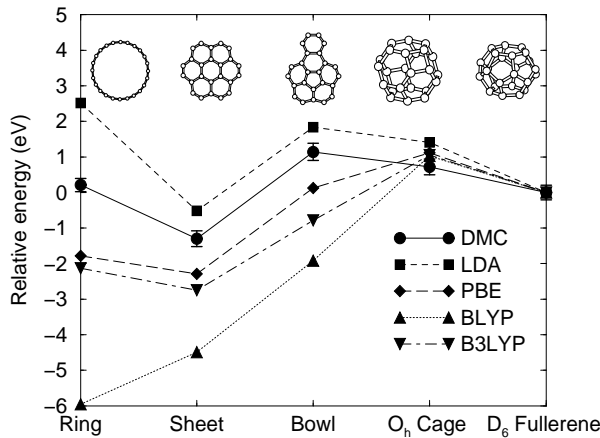


FIG. 1. The structures and energies of the  $C_{24}$  isomers given relative to the  $D_6$  fullerene.

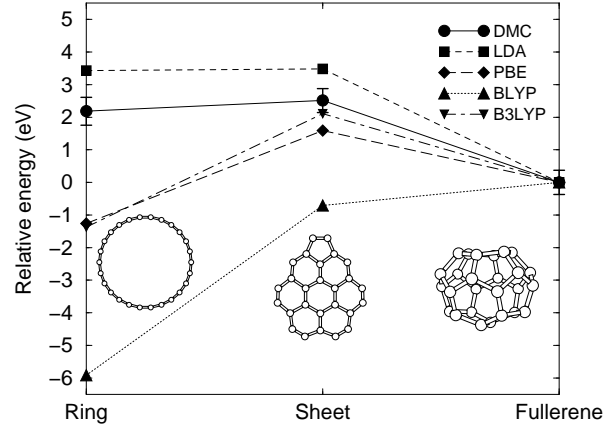


FIG. 2. The structures and energies of the  $C_{26}$  isomers, given relative to the fullerene.

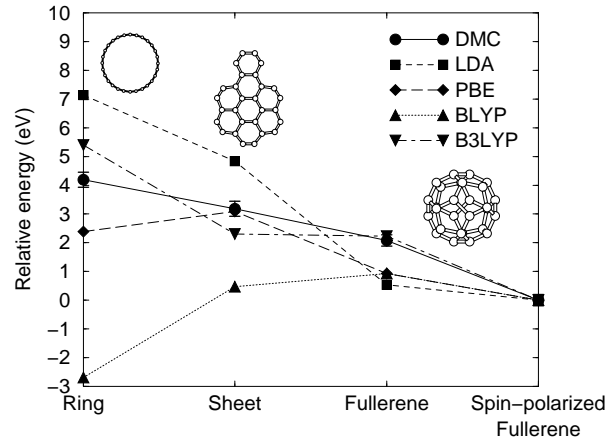


FIG. 3. The structures and energies of the  $C_{28}$  isomers, given relative to the spin-polarized fullerene (see text).

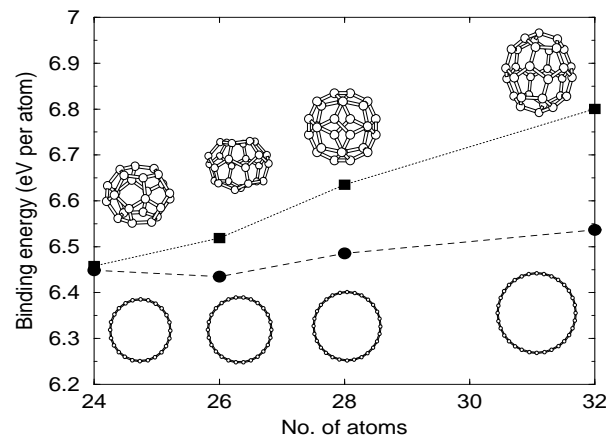


FIG. 4. The DMC binding energies of the  $C_{24}$ ,  $C_{26}$ ,  $C_{28}$ ,  $C_{32}$  ring and fullerene structures. The lines drawn are for guidance only. Statistical error bars are smaller than the symbols.